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(54) METHODS OF DISSOLVING CELLULOSE ETHERS IN ALKALINE MEDIA

(71) We, HERCULES INCORPORATED, a Corporation organised under the laws of the State of Delaware, United States of America, of 910 Market Street, City of Wilmington, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to water-soluble cellulose ethers and in particular to cellulose ethers which have a reduced tendency to agglomerate in high pH aqueous media.

Several water-soluble cellulose ethers are commercially available, but in several cases the rate of dissolution is very slow. This is caused by the fact that when such an ether particle touches the water the outer surface will swell and form a gel which dissolves slowly. If a mass of particles touches the water more or less simultaneously, the particles swell and gel and stick to neighboring particles, thus forming an agglomerate which dissolves even slower than the gel formed by one particle alone.

It is known that treatment of water-soluble cellulose ethers with a cross-linking material such as an aldehyde or dialdehyde improves the dispersibility of that ether in water. When such a treated cellulose ether is added to water and stirred, there is a time interval from the moment the ether is added until the moment solution viscosity begins to develop. This time, known as the hydration time, is thought to be a measure of the time required for water to hydrolyze hemiacetal cross linkages produced by interaction of the aldehyde or dialdehyde with the cellulose ether. During the hydration period, water penetrates to the interior of the individual particles without causing the surfaces to become sticky. When these cross linkages are broken, the cellulose ether dissolves, causing the solution viscosity to increase. Complete solution of such an ether is evidenced by the attainment of a stable solution viscosity.

The aldehyde or dialdehyde treated cellulose

ethers are known to dissolve with little or no tendency to lump or agglomerate in neutral, weakly alkaline or acidic aqueous media, and to attain stable solution viscosity, but in strongly alkaline or high pH aqueous systems, e.g., about pH 10 or equivalent, agglomeration occurs and solution viscosity does not develop smoothly, probably because hydration occurs too rapidly.

By means of the present invention it is possible to dissolve a cellulose ether in high pH systems and avoid the agglomeration normally experienced in forming such solutions.

According to the invention there is provided a method of improving the dispersibility of a cellulose ether in an aqueous liquid having a pH greater than 10 which comprises contacting particulate cellulose ether with boric acid or a water-soluble borate in the presence of a solvent for said boric acid or borate, removing the solvent and drying the residue. The dried residue may then be added to the high pH aqueous liquid to form a dispersion. The cellulose ether may also have been modified by treatment with an organic compound which forms hemiacetal bonds with said cellulose ether as discussed above, depending on the results desired. The preferred hemiacetal bond forming organic compounds are polyfunctional aldehydes. The most suitable organic compound is glyoxal.

The treatment of the cellulose ether with the boric acid or borate is preferably carried out in nonacidic, preferably alkaline medium. In a suitable method boric acid or a borate is added to a slurry of cellulose ether and organic liquid, and after mixing, the liquid is removed and the solid residue is dried. The preferred organic liquid is acetone, and an alkali such as sodium hydroxide or an amine such as monoethanolamine is preferably also present.

The treatment of a cellulose ether with both a polyfunctional aldehyde and boric acid or a borate should preferably be carried out in a nonalkaline, preferably acidic,

medium. Preferred methods of treatment are as follows:

(I) Boric acid or a borate is added with a polyfunctional aldehyde to a water-miscible organic liquid, a cellulose ether is then added and the whole mixed thoroughly, the supernatant liquid removed and the solid residue dried.

(II) A polyfunctional aldehyde is added to a cellulose ether/acidified organic liquid slurry. After mixing, boric acid or a borate is added and the whole is further mixed, after which it is filtered and the solid residue dried.

(III) A polyfunctional aldehyde is added to a cellulose ether/acidified organic liquid slurry. The whole is mixed and the supernatant liquid is removed. Boric acid or a borate in solution is added to the moist residue and after mixing the resultant mass dried.

(IV) A polyfunctional aldehyde is added to a cellulose ether/acidified organic liquid slurry, the whole is mixed, filtered and the residue dried. The treated residue is reslurried with further water-soluble organic liquid, boric acid or borate is added, the liquid is removed, and the resultant mass dried.

The preferred cellulose ether is hydroxyethyl cellulose. Other examples are methyl cellulose, methylhydroxypropyl cellulose, methylhydroxyethyl cellulose and ethylhydroxyethyl cellulose.

It is important that the boric acid or borate be added in solution form to the cellulose ether slurry and that the dissolving liquid be removed substantially completely. The mechanism by which the unique and unexpected effect of this invention takes place is unknown, i.e., whether it is a reaction between the borate and ether or simply a deposition of the borate on the particle. In either event, the effect takes place in or from solution only. Upon drying, the resultant product is readily soluble in high pH aqueous systems without agglomeration. The treated and dried cellulose ether is normally ground to a fine particle size for use.

The borate will normally be a readily soluble borate, e.g., borax, potassium borate or ammonium borate, and the solvent can be either water or a suitable organic solvent such as methanol. The preferred dialdehyde is glyoxal and the preferred organic liquid is acetone. The dialdehyde is preferably water-soluble and used in aqueous solution for application to the cellulose ether slurry.

It is preferred that the dialdehyde be present in the reaction mixture within the concentration range 0.005 to 5% by weight based on the cellulose ether, suitably 0.04 to 2.0%. It is preferred that the boric acid or borate be present within the concentration range 0.001 to 0.5% by weight based on the cellulose ether, suitably 0.003 to 0.2%, when a dialdehyde is also used. When boric acid or borate is used alone, the preferred maximum proportion is 5%, suitably 2%.

The invention is illustrated by means of the following examples, in which the cellulose ether used is in particulate form.

EXAMPLE 1

To 25 g. of hydroxyethyl cellulose (HEC) were added 60 cm.³ of acetone, 6.25 cm.³ of a solution of 40 g. borax in 1 dm³ of methanol, 8 cm.³ of 0.1M sodium hydroxide solution. The whole was mixed and dried on a water bath. After grinding the dried product, it was added at 2% concentration to the filtrate of a slurry of 250 g. of Portland cement in 1 dm³ of water and the hydration time and viscosity development of the mixture was observed. The filtrate of Portland cement had a pH > 12.

The hydration time was 7 minutes and no agglomeration was observed, the viscosity developing smoothly as soon as the treated hydroxyethyl cellulose was mixed with the high pH system. The viscosity was measured with a Brabender Visco Corder Model VC-3.

EXAMPLES 2 to 4

The method used for each example was the same as in Example 1. The quantities used and the results obtained are as follows:

Example No.	HEC (g)	Acetone (cm ³)	Borax Soln. (cm ³) 40 g/dm ³ in Methanol	0.1M NaOH	Hydration Time (Mins.)
2	25	60	12.5	8	7
3	25	60	6.25	3.2*	6
4	25	60	4	8	4

* 0.5 NaOH was used in this example

In all cases no agglomeration was observed and the viscosity developed smoothly.

EXAMPLE 5

To 500 g. of moist hydroxyethyl cellulose

were added 2 dm³ of acetone. The hydroxyl cellulose-acetone system was acidified with acetic acid, the acid value (as herein after defined) being adjusted to 24, and the desired amounts of glyoxal and borax

were added at 30°C. The term "acid value" is defined as the number of cm.³ of 0.1M NaOH required to neutralize 100 cm.³ of acidified acetone. Glyoxal was added as a 40% aqueous solution, the amount added being 0.25% by weight of 100% glyoxal based on the weight of hydroxyethyl cellulose. Aqueous sodium borate was added as a 4.5% strength solution, the amount added being 0.1% by weight of borax as Na₂B₄O₇ · 10H₂O based on the weight of hydroxyethyl cellulose. The mass was stirred for 30 minutes and then suction filtered. The treated hydroxyethyl cellulose was dried on a steam bath at 90°–100° for 2 hours.

After grinding the product, it was added to the filtrate of a slurry of 250 g. Portland

cement, Grade A, in 1dm³ of water, and the hydration time and viscosity development of the mixture was observed. The filtrate of Portland cement slurry had a pH > 12.

The hydration occurred immediately and no agglomeration was observed. The viscosity developed smoothly as soon as the treated hydroxyethyl cellulose was mixed with the high pH aqueous system. The viscosity was measured with a Brabender Visco Corder Model VC-3.

EXAMPLES 6 to 8

The method used was the same as in Example 1. The following results were obtained, the percentages of glyoxal and borax being based on the weight of hydroxyethyl cellulose.

Example No.	% Glyoxal	% Borax	Acid Value	Hydration Time at pH > 12
6	.04	0.10	24	—
7	.10	0.02	24.8	½ min.
8	.10	0.07	24.8	—

In all cases, no agglomeration was observed and the viscosity developed smoothly.

and the viscosity developed smoothly thereafter. No agglomeration was observed.

EXAMPLE 9

To 500 g. of moist hydroxyethyl cellulose were added 2 dm³ of acetone. 0.15% by weight of glyoxal based on the weight of hydroxyethyl cellulose was added at 30°C., the glyoxal being a 40% aqueous solution. The whole was mixed for 30 minutes and the supernatant liquid was siphoned off leaving a moist cake of glyoxal treated hydroxyethyl cellulose.

Aqueous sodium borate was added as a 4.5% strength solution, the amount added being 0.03% by weight of borax as Na₂B₄O₇ · 10H₂O based on the weight of hydroxyethyl cellulose. The cake was dried on a steam bath at 90–100° for 2 hours.

After grinding the product, 25 g. was added to 200 cm.³ of the filtrate of a slurry of 250 g. Portland cement Grade A in 1dm³ of water, and the hydration time and viscosity development of the mixture were observed. The hydration time was 2 minutes

EXAMPLE 10

To 400 g. of acetone was added to 2.25% strength aqueous sodium borate solution and 40% glyoxal solution sufficient to give .0056% by weight of sodium borate and 0.1% by weight glyoxal, both based on the weight of hydroxyethyl cellulose used. To this mixture was added 100 g. of hydroxyethyl cellulose and the whole mixed for 15 minutes. The supernatant liquid was siphoned off, the treated residue dried and pulverized. The pulverized residue was added to a sample of water at pH 12, produced by filtering a slurry of 250 g. of cement with 1dm³ of water, and the hydration time (as hereinbefore defined) and solution time were both measured with a Brabender Visco Corder Model VC-3. The solution time is the time taken to reach stable solution viscosity. The solution viscosities were seen to develop smoothly with no observable agglomeration occurring.

Result

% Glyoxal	% Borax	Hydration Time at pH 12	Solution Time at pH 12
0.1	.0056	2.5 minutes	19.0 minutes

EXAMPLES 11 to 15

The methods used were substantially the same as in Example 10. No agglomeration was observed in any example.

Results

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Example No.	% Glyoxal	% Borax	Hydration Time at pH 12 (Minutes)	Solution Time at pH 12 (Minutes)
10				
11	.12	.0068	1.4	18.0
12	.16	.0056	2.5	35.0
13	.24	.0056	3.1	21.5
14	.28	.0056	2.5	16.1
15	1.00	.0034	1.3	25.5

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EXAMPLES 16 to 20

The methods used were substantially the same as in Example 10 except that hydroxyethyl cellulose samples of lower molecular weight (Examples 16 and 17 with a 2%

Brookfield viscosity of 320 and Examples 18, 19 and 20 with a 2% Brookfield viscosity of about 2000) were employed. No agglomeration was observed in dissolving 5 g. of any of the treated samples in 200 ml. of water having a pH >12.

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Example No.	HEC Type	% Glyoxal	% Borax	Hydration Time Minutes	Solution Time Minutes
30					
16	150 K	1.0	0.07	0.5	20
17	150 K	1.0	0.09	0.5	40
18	150 G	1.2	0.1	0.5	11
19	150 G	1.0	0.22	0	90
35	20	150 G	2.0	0.22	300

EXAMPLE 21

To 50 g. of hydroxyethyl cellulose was added 100 cm³ of acetone and 1 cm³ of 1M NaOH. The required amount of borax solution was added as a 4.5% aqueous solution. The supernatant liquid was removed and the residue was dried at about 90°C. Hydration time was measured with a Brabender Visco Corder in aqueous solutions at pH 12. The

pH 12 medium was provided by filtering a slurry of 250 g. of Portland cement Grade A and 1dm³ of water.

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This procedure was followed with 0.09, 0.18 and 0.27% borax (based on the hydroxyethyl cellulose). No agglomeration was observed and smooth viscosity development was achieved in all cases.

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The results are tabulated as follows:—

Amount of Borax	Hydration Time at *Alkali Value 10	Hydration Time at *Alkali Value 20
0.09	2 minutes	$\frac{1}{2}$ minute
0.18	3 minutes	2 minutes
0.27	3 minutes	3 $\frac{1}{2}$ minutes
*Alkali value is defined as cc. of 0.1M HCL required to neutralize 100 cc. of alkaline acetone		

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EXAMPLE 22

Ten grams dry basis of hydroxyethyl cellulose was slurried in 100 ml. of acetone at room temperature. Then 20 ml. of aqueous solution (prepared by mixing 6 ml. of 1% borax (Na₂B₄O₇·10H₂O) solution with 14 ml. of water) was added dropwise with stirring over 20 minutes. Agitation was continued for one hour at ~25°C. Then excess liquid was removed by filtration and the product was washed with three 50 ml. portions of acetone to remove water. Excess acetone was removed by filtration and the

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product was dried in vacuo at 60°C. for one hour.

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The product had good dispersibility in 0.01N NaOH solution at pH 12. The hydration time was 1.2 minutes followed by a fast increase in viscosity to 880 cps. A maximum viscosity of 920 cps. was attained in about 20 minutes.

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EXAMPLE 23

The procedure of Example 22 was repeated except that the 20 ml. of solution added dropwise was prepared by mixing

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2.5 ml. of boric acid solution with 17.5 ml. of water. After water was removed by washing with two 50 ml. portions of acetone, and excess acetone removed by filtration, the product was dried in vacuo at 60°C. for one hour.

The product had good dispersibility in 0.01 NaOH solution at pH 12. The hydration time was one minute, followed by a fast increase in viscosity to 660 cps. in five minutes and 700 cps. in ten minutes. A maximum viscosity of 740 cps. was attained in about 35 minutes.

EXAMPLE 24

The procedure of Example 22 was repeated except that the 20 ml. of solution added dropwise was prepared by mixing 1 ml. of 1% glyoxal solution and 2 ml. of 1% borax solution with 17 ml. of water. After removal of excess acetone by filtration, the product was air dried overnight.

The product has good dispersibility in 0.01N NaOH solution at pH 12 but dissolved slowly. The hydration time was about 12 minutes, followed by a very slow rise in viscosity to 150 cps. in 50 minutes.

EXAMPLE 25

One hundred grams of hydroxyethyl cellulose was slurried in 1200 grams of acetone (acetone:water 97:1). Dry boric acid (0.30% by weight on cellulosic) was added to this slurry. After stirring for 10 minutes monoethanol amine (0.30% by weight on the cellulose derivative) was added. After stirring for another 20 minutes the product was dried in a ventilated oven at 70°C. for 30 minutes. The hydration time of the product was 2 minutes, the dissolving time was 11 minutes at pH 13.

WHAT WE CLAIM IS:—

1. A method of improving the dispersibility of a cellulose ether in an aqueous liquid having a pH greater than 10 which comprises contacting particulate cellulose

ether with boric acid or a water-soluble borate in the presence of a solvent for said boric acid or borate, removing the solvent and drying the residue.

2. A method according to claim 1 wherein the boric acid or borate is present within the concentration range of 0.001 to 5% by weight, based on the weight of cellulose ether.

3. A method according to claim 1 wherein the cellulose ether is treated also with a dialdehyde in the amount of 0.005 to 5% by weight based on the weight of cellulose ether.

4. A method according to claim 3 wherein the dialdehyde is present in the amount of 0.04 to 2% by weight.

5. A method according to claim 3 or 4 wherein the amount of boric acid or borate is 0.003 to 0.2% by weight based on the weight of cellulose ether.

6. A method according to any one of claims 3 to 5 wherein the dialdehyde is glyoxal.

7. A method according to claim 1 or 2 wherein the solvent for boric acid or borate is alkaline.

8. A method according to any one of claims 3 to 6 wherein the solvent for boric acid or borate is acidic.

9. A method of improving the dispersibility of a cellulose ether in aqueous liquid having a pH greater than 10 substantially as hereinbefore described with reference to the Examples.

10. Dried cellulose ether residues whenever produced by a method according to any one of claims 1 to 9.

11. Aqueous systems having a pH greater than 10, containing dispersed cellulose ether, whenever produced by a method according to any one of claims 1 to 9.

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